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**Synthesis, Characterization, and Theoretical Considerations of 1, 2-**  
**bis(oxyamino)ethane Salts**

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**Abstract:** The synthesis, characterization, theoretical calculations, and safety studies of energetic salts of 1,2-bis(oxyamino)ethane, (H<sub>2</sub>N-O-CH<sub>2</sub>-CH<sub>2</sub>-O-NH<sub>2</sub>), were carried out. The salts were characterized by vibrational (infrared, Raman), multinuclear nmr studies (<sup>1</sup>H, <sup>13</sup>C), differential scanning calorimetry (DSC); elemental analysis; and initial safety testing (impact and friction sensitivity). Theoretical calculations on the neutral, monoprotonated, and doubly protonated species of ethylene bisoxyamine were carried out using xxxx level of theory for the lowest energy structure and these theoretical results compared with the experimentally observed bond distances and vibrational (ir, Raman) frequency values. The single crystal x-ray diffraction study was carried out on the mono-perchlorate salt revealing a high degree of hydrogen bonding with an unexpected structure.

**Introduction**

At the Air Force Research Laboratory the quest for new low melting salts is an ongoing process. We have pursued synthetic endeavors with salts especially ionic liquids for several reasons; (1) The materials are often more dense than their corresponding

neutral analogues; (2) Salts have essentially no vapor pressure at ambient working conditions making their handling significantly more facile, since there is little concern for vapor toxicity; and (3) Salts are often soluble in a wide array of commonly available polar solvents making synthesis, characterization and isolation significantly easier.

Synthetically, electron poor oxyamine synthons such as  $\text{CF}_3\text{-SO}_2\text{-O-NH}_2$  or  $[(\text{NO}_2)_3\text{C}_6\text{H}_2\text{-O-NH}_2]$  have been used in their neutral form to transfer formally an "NH<sub>2</sub><sup>+</sup>" group to substituted amine group forming the corresponding hydrazine.<sup>1-4</sup> Systems containing multiple oxyamine functionalities,  $\text{H}_2\text{N-O-R-O-NH}_2$ , have not been widely investigated as salt systems whereby the terminal amine functionalities have been protonated by various acids. The oxyamine functionality,  $\text{-O-NH}_2$ , which is the oxo analogue of the hydrazine group,  $\text{-NH-NH}_2$ , and is a very desirable functionality from the viewpoint of its oxygen content as well as its relative high heat of formation. Previously we reported the synthesis and characterization of highly oxygenated salts based upon methylene bisoxyamine ( $\text{H}_2\text{N-O-CH}_2\text{-O-NH}_2$ ) that revealed interesting results despite the dramatic property of unexpected and untimely deflagrations of several of the salts upon standing at ambient conditions for extended periods of time.<sup>5</sup> One consideration was that a single carbon atom geminally substituted with oxyamine functions could be unstable. Therefore we decided to investigate the ethyl analogue, 1, 2-bis(oxyamino)ethane, in which each carbon center has only one oxyamine attachment with the hypothesis that the system might be more robust. Herein we report on the properties of this family of salts several of which fall under the well accepted definition of an ionic liquid<sup>6-9</sup>.

**Experimental.** Although no incidents were encountered in the synthesis and characterization in any of the energetic salts of ethylene bisoxyamine, many of these materials are extremely sensitive to both friction and impact. Blast shields, tongs, safety glasses, full-face shields, leather aprons, jackets, chaps and heavy duty leather gloves were used during all manipulations. Caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials. Also, mechanical actions involving scratching or scraping should be avoided. 1, 2-bis(oxyamino)ethane, ethylene bis(oxyamine), was prepared through the literature route<sup>10</sup>. Once prepared it was stored under a nitrogen atmosphere in a Schlenk flask until needed. It could be

crystallized with much difficulty, but significant mass losses were encountered, and it was found that this extra purification was not necessary. Nitric acid,  $\text{HNO}_3$  (69-70% by weight aqueous solution; A.C.S. reagent grade) was purchased from Aldrich Chemical Company and used without further purification. Perchloric acid,  $\text{HClO}_4$  (70.0% by weight aqueous solution; Baker Reagent grade) was used as received. Ammonium dinitramide,  $\text{NH}_4\text{N}(\text{NO}_2)_2$ , was graciously donated from ATK Thiokol, Inc., and after Raman spectroscopy showed low  $\text{NO}_3^-$  content, it was stored in a brown bottle inside a nitrogen filled glove box. Methanol,  $\text{CH}_3\text{OH}$ ; ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ ; and 2-propanol,  $(\text{CH}_3)_2\text{CH-OH}$ , (ACS reagent grade; Aldrich Chemical Company) were distilled from sodium metal and degassed using a liquid nitrogen freeze-thaw vacuum procedure. Ethyl acetate, A. C. S. reagent grade was used as received. All solvents were stored inside glass vessels, which were sealed with Teflon screw-cap plugs and were equipped with #15 O-ring fittings. Infrared spectra were recorded as KBr disks from 4000-400  $\text{cm}^{-1}$ , (using a KBr disk as a reference background) on a Nicolet 55XC FT-IR spectrometer. Raman spectra were recorded in pyrex melting point capillaries on Bruker Model FRA 106/S Equinox 55 Raman spectrometer equipped with a 1.06 micron IR excitation laser. NMR experiments were carried out by dissolving the salts in  $\text{CD}_3\text{OD}$  in 5mm nmr tubes, and the  $^1\text{H}$  and  $^{13}\text{C}$  spectra recorded on a Bruker Spectrospin DRX 400 MHz Ultrashield<sup>TM</sup> NMR. Thermal analyses were carried out in hermetically sealed, coated aluminum pans on a Thermal Analyst 200, Dupont Instruments 910 Differential Scanning Calorimeter. Samples were prepared and sealed inside a nitrogen-filled glove box, and once the pans were inside the DSC cell, the cell was flushed with 10 mL per minute of nitrogen gas purge during heating cycles. Elemental analyses were carried out by Galbraith Laboratories, Inc., of Knoxville, TN.

Ethylene bis(oxyamine) mononitrate  $[\text{NH}_2\text{-O-CH}_2\text{-CH}_2\text{-O-NH}_3^+][\text{NO}_3^-]$ : A preweighed Schlenk flask was charged with ethylene bis(oxyamine), 0.7222 g.; 7.84 mmol) under a brisk flow of nitrogen gas, followed by the addition of ethanol, 10 ml and a Teflon stir bar. Upon dissolution of the ethylene bis(oxyamine) into the ethanol, nitric acid (0.6620g, 7.35 mmol) was added to the vigorously stirred, colorless, homogenous solution with a pre-weighed pipet. The reaction was allowed to stir an additional 20 minutes at ambient

temperature. At the end of this time, the Teflon stir bar was removed and 40 ml of diethyl ether was carefully layered upon the concentrated reaction solution. Upon storage at 4° C for 48 hours, a large crop of white crystalline material was deposited. The solution was decanted away and the crystals washed with three (25 mL) aliquots of diethyl ether, and then were vacuum dried leaving 1.048 g of ethylene bis(oxyamine) mononitrate (88% of theory). Melting point (DSC): 73-76° C.

Infrared ( $\text{cm}^{-1}$ ): 3225, 3123, 2980, 2954, 2745, 2402, 2157, 2044, 1594, 1582, 1540, 1528, 1471, 1386, 1230, 1208, 1078, 1052, 990, 854, 841, 825, 618, 592, 473, 440.

Raman ( $\text{cm}^{-1}$ ): 3340, 3257, 2990, 2969, 2949, 2894, 2866, 2789, 1650, 1582, 1536, 1461, 1443, 1407, 1320, 1283, 1251, 1229, 1096, 1049, 1043, 992, 932, 914, 852, 829, 813, 732, 717, 706, 574, 490, 450, 384, 277, 227, 136, 112, 85.

$^1\text{H}$  nmr ( $\text{CD}_3\text{OD}$ , ppm): 4.30 (singlet); 5.02 (singlet, broad)

$^{13}\text{C}$  nmr ( $\text{CD}_3\text{OD}$ , ppm): 73.74

Elemental analysis: theory; %C, 15.48, %H, 5.84, %N, 27.09; no satisfactory elemental obtained.

Ethylene bis(oxyamine) dinitrate.  $[\text{NH}_3\text{-O-CH}_2\text{-CH}_2\text{-O-NH}_3^{2+}][\text{NO}_3^-]_2$ : A preweighed Schlenk flask was charged with ethylene bis(oxyamine), 0.7072 g, 7.68 mmoles, under a brisk flow of nitrogen gas, followed by the addition of 15 mL of ethanol and a Teflon stir bar. To the homogenous, vigorously stirred solution, nitric acid (1.4594 g, 16.2 mmoles) was added with a preweighed pipet. The reaction solution was allowed to stir overnight at room temperature. The next day the Teflon stir bar was removed and the reaction solution carefully layered with diethyl ether, 25 mL, under a brisk nitrogen flow. The reaction flask was then sealed and placed in a refrigerator at 4°C for 24 hours, whereupon, a large crop of white crystalline blocks was deposited. The mother solution was decanted away, and the crystals washed with diethyl ether, three (15 mL) aliquots, and then vacuum dried to a constant mass, 1.2799 g of ethylene bis(oxyamine) dinitrate (76% of theory). Melting point (DSC): 133-135°C

Infrared ( $\text{cm}^{-1}$ ): 3300-2500 broad, strong, 3071, 2967, 2759, 2708, 1599, 1564, 1510, 1418, 1384, 1308, 1227, 1183, 1095, 1059, 1038, 1025, 984, 932, 830, 823, 810, 522, 476.

Raman ( $\text{cm}^{-1}$ ): 3300-2500 broad, medium, 2995, 2952, 2780, 2704, 1649, 1584, 1551, 1441, 1325, 1305, 1245, 1192, 1095, 1043, 1021, 932, 830, 809, 932, 829, 809, 732, 708, 473, 451, 257, 137, 110, 84, 73, 56.

$^1\text{H}$  nmr ( $\text{CD}_3\text{OD}$ , ppm): 4.34 (singlet); 5.06 (singlet, broad)

$^{13}\text{C}$  nmr ( $\text{CD}_3\text{OD}$ , ppm): 73.55

Elemental analysis: theory; %C, 11.01, %H, 4.62, %N, 25.68; Found; %C, 11.28, %H, 4.56, %N, 24.69.

Ethylene bis(oxyamine) monoperchlorate  $[\text{NH}_2\text{-O-CH}_2\text{-CH}_2\text{-O-NH}_3^+][\text{ClO}_4^-]$ : A preweighed Schlenk flask was charged with ethylene bis(oxyamine) (0.7752 g; 8.42 mmol) under a brisk flow of nitrogen gas, followed by the addition of ethanol, 10 ml, and a Teflon stir bar. Upon dissolution of the ethylene bis(oxyamine) into the ethanol, perchloric acid (1.1388g, 7.93 mmol) was added to the vigorously stirred, colorless, homogenous solution with a pre-weighed pipet. The reaction was allowed to stir an additional 20 minutes at ambient temperature whereupon the Teflon stir bar was removed and diethyl ether, 15 ml, was carefully layered upon the concentrated reaction solution. Storage at  $4^\circ\text{C}$  for 48 hours resulted in a large crop of white crystalline material and the solution was layered with an additional 20 mL of diethyl ether and stored at  $4^\circ\text{C}$  for 24 hours more. The solution was decanted away from the large crop of white crystals which were then washed with three (25 mL) aliquots of diethyl ether and then were vacuum dried leaving 1.5133 g of ethylene bis(oxyamine) monoperchlorate (99% of theory).

Melting point (DSC):  $134\text{-}137^\circ\text{C}$ .

Infrared ( $\text{cm}^{-1}$ ): 3326, 3254, 3225, 3126, 2978, 2960, 2934, 2758, 2747, 2037, 1580, 1565, 1471, 1428, 1385, 1327, 1276, 1233, 1087, 1054, 992, 970, 941, 862, 855, 842, 625, 519, 463.

Raman ( $\text{cm}^{-1}$ ): 3320, 3252, 3006, 2977, 2954, 2931, 2837, 2760, 2699, 1580, 1429, 1137, 1069, 937, 862, 768, 626, 459, 375, 177, 107, 84.

$^1\text{H}$  nmr ( $\text{CD}_3\text{OD}$ , ppm): 4.06 (singlet), 5.09 (broad singlet)

$^{13}\text{C}$  nmr ( $\text{CD}_3\text{OD}$ , ppm): 75.08

Elemental analysis: theory; %C, 12.47, %H, 4.71, %N, 14.54; Found; %C, 12.43, %H, 4.68, %N, 14.33.

Ethylene bis(oxyamine) diperchlorate  $[\text{NH}_3\text{-O-CH}_2\text{-CH}_2\text{-O-NH}_3^{2+}][\text{ClO}_4^-]_2$ : A preweighed Schlenk flask was charged with ethylene bis(oxyamine) (0.5470g; 5.94 mmol) under a brisk flow of nitrogen gas, followed by the addition of ethanol, 10 mL, and a Teflon stir bar. Upon dissolution of the ethylene bis(oxyamine), perchloric acid (1.7319g, 12.0 mmol) was added to the vigorously stirred, colorless, homogenous solution with a pre-weighed pipet. The reaction was allowed to stir an additional 20 minutes at ambient temperature. At the end of this time, the Teflon stir bar was removed and 25 mL of diethyl ether carefully layered upon the concentrated reaction solution. Subsequent storage of the solution at 4°C overnight resulted only in a homogenous clear solution, which was vacuum stripped to dryness leaving a white solid. This solid was dissolved in 10 mL of acetonitrile, which was then carefully layered with 40 mL of diethyl ether, followed by storage of the flask at 4°C for 24 hours. A large crop of white crystalline material was deposited, which was washed with three (15 mL) aliquots of diethyl ether followed by drying under high vacuum, resulting in 1.3077 g of ethylene bis(oxyamine) diperchlorate (84% of theory). Melting point (DSC): 137°C. Infrared ( $\text{cm}^{-1}$ ): 3400-2600 broad, strong, 3199, 3124, 3073, 2997, 2987, 2778, 2686, 2655, 1656, 1585, 1570, 1534, 1510, 1447, 1434, 1365, 1105, 1087, 1032, 927, 843, 826, 809, 636, 625, 549. Raman ( $\text{cm}^{-1}$ ): 3250-3050 broad, 3126, 3009, 2985, 2950, 2892, 2806, 2714, 1575, 1558, 1515, 1459, 1431, 1310, 1243, 1143, 1105, 1043, 1003, 960, 938, 844, 809, 636, 625, 549, 470, 455, 383, 84.  $^1\text{H}$  nmr ( $\text{CD}_3\text{OD}$ , ppm): 4.33 (singlet); 5.07 (broad singlet)  $^{13}\text{C}$  nmr ( $\text{CD}_3\text{OD}$ , ppm): 73.40 Elemental analysis: theory; %C, 8.19, %H, 3.43, %N, 9.56; Found; %C, 8.19, %H, 3.45, %N, 9.34.

Ethylene bis(oxyamine) monodinitramide  $[\text{NH}_2\text{-O-CH}_2\text{-CH}_2\text{-O-NH}_3^+][\text{N}(\text{NO}_2)_2^-]$ : This reaction was carried out in the dark with only the assistance of a red flashlight. Ethylene bis(oxyamine), 0.7250 g, 7.87 mmol, was added to a 1000 mL round bottom flask and dissolved in 100 mL of fresh methanol. Ammonium dinitramide,  $[\text{NH}_4][\text{N}(\text{NO}_2)_2]$ ,



0.9646 g, 7.78 moles, was dissolved in 30 mL of fresh methanol and then poured onto the top of a column containing Amberlyst 15 Resin (strong cation  $H^+$  exchange resin, Supelco, Inc.). This resin bed (1.25" X 14") had been previously activated with 1M hydrochloric acid solution followed by a solvent change from pure water to pure methanol. The ammonium dinitramide solution was slowly eluted through this column at 1 to 2 drops per second into the flask containing vigorously stirred ethylene bis(oxyamine) solution. As the solvent volume above the resin bed became minimal, 100 mL of fresh methanol was added to the top of the column and elution continued. This process was repeated 4 times to assure complete elution of the protonated dinitramide solution through the resin bed. The resultant reaction solution was then rotary evaporated leaving a viscous straw colored oil. This oil was then transferred with a minimal amount of methanol to a pre-weighed Shlenk vessel and subsequently evacuated. Ethyl acetate, 15 mL, was added and partially dissolved the oil. The ethyl acetate was then removed by high vacuum resulting in the rapid crystallization of the product salt. The crystals were dissolved in dry ethanol, 10 mL, and layered with diethyl ether, 40 mL, and stored at 4° C overnight. A large crop of white crystals was deposited, which was washed with three (10 mL) aliquots of diethyl ether and vacuum dried, resulting in 1.5354 grams of ethylene bis(oxyamine) monodinitramide (97% of theory).

Melting point (DSC): 55-59°C.

Infrared ( $cm^{-1}$ ): 3296, 3224, 3123, 2980, 2965, 2885, 2743, 1593, 1538, 1472, 1434, 1384, 1363, 1344, 1225, 1207, 1178, 1076, 1054, 1033, 1021, 989, 963, 953, 854, 841, 827, 761, 732, 589.

Raman ( $cm^{-1}$ ): 3293, 3230, 2946, 2928, 2879, 2811, 2727, 1597, 1517, 1459, 1329, 1263, 1233, 1222, 1168, 1116, 1076, 1059, 1011, 964, 860, 826, 759, 744, 590, 484, 404, 296, 118, 84, 75, 62.

$^1H$  nmr ( $CD_3OD$ , ppm): 4.08 (singlet), 5.05 (singlet broad)

$^{13}C$  nmr ( $CD_3OD$ , ppm): 75.02

Elemental analysis: theory; %C, 12.06, %H, 4.55, %N, 35.17; Found; %C, 12.08, %H, 4.30, %N, 34.21.



Ethylene bis(oxyamine) bis(dinitramide)  $[\text{NH}_3\text{-O-CH}_2\text{-CH}_2\text{-O-NH}_3^{2+}][\text{N}(\text{NO}_2)_2^-]_2$ : The synthesis procedure was carried out in essentially the same manner as that described for the mono dinitramide salt. Ethylene bis(oxyamine), 0.6208 g, 6.74 mmol, was added to a 1000 mL round bottom flask and dissolved in 100 mL of fresh methanol. Ammonium dinitramide,  $[\text{NH}_4][\text{N}(\text{NO}_2)_2]$ , 1.6700 g, 13.46 mmol, was dissolved in 30 mL of fresh methanol and then poured onto the top of column containing Amberlyst 15 Resin (strong cation  $\text{H}^+$  exchange resin, Supelco, Inc.). The ammonium dinitramide solution was slowly eluted through this column at 1 to 2 drops per second into the flask containing the vigorously stirred ethylene bis(oxyamine) solution. The resin bed was eluted with an additional three (100 mL) aliquots of fresh methanol assuring complete elution of the protonated dinitramide. The resultant reaction solution was then rotary evaporated down to leave a viscous straw colored ionic liquid, which was transferred with a minimal amount of methanol to a preweighed Schlenk vessel and evacuated. Ethyl acetate, 15 mL, was added, dissolving the ionic liquid. The solution was carefully layered with 20 mL of diethyl ether. Storage at  $4^\circ\text{C}$  for one week, followed by the addition of 30 mL more of diethyl ether, resulted in the recovery of a viscous straw colored ionic liquid, which was evacuated to a constant weight at  $4 \times 10^{-3}$  torr, 1.6016 grams (78% theory).

Infrared ( $\text{cm}^{-1}$ ): 3350- 2350 broad strong, 3150- 2950 very strong, 2727, 2687, 2356, 1984, 1533, 1428, 1348, 1196, 1030, 962, 838, 824, 765, 731, 572, 559, 461.

Raman ( $\text{cm}^{-1}$ ): 3300- 2700 broad medium, 3002, 2956, 2886, 1570, 1520, 1329, 1190, 1103, 1046, 1000, 959, 826, 760, 489, 386, 306, 85.

$^1\text{H}$  nmr ( $\text{CD}_3\text{OD}$ ): 4.39 (singlet), 6.37 (broad singlet).

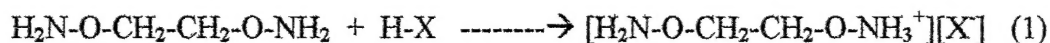
$^{13}\text{C}$  nmr ( $\text{CD}_3\text{OD}$ ): 73.57

Elemental analysis: theory; %C, 7.84, %H, 3.29, %N, 36.60; Found; %C, 7.73, %H, 3.66, %N, 34.62.

### General Discussion.

The synthesis and isolation of the nitrate and perchlorate salts was very straightforward and involved the reaction of one mole equivalent of the commercially

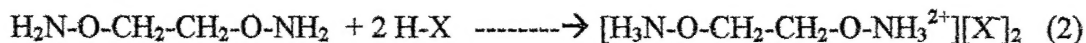
available concentrated acid with one mole equivalent of ethylene bis(oxyamine) to make the desired mono-protonated salts (Equation 1).



Where  $\text{H-X} = \text{HNO}_3, \text{HClO}_4, \text{ or "HN(NO}_2)_2"$

$\text{X}^- = \text{NO}_3^-, \text{ClO}_4^-, \text{ or N(NO}_2)_2^-$

For the synthesis of the doubly protonated salts, two mole equivalents of concentrated acid were reacted with one mole of ethylene bis(oxyamine) to make the double salts (Equation 2).



Where  $\text{H-X} = \text{HNO}_3, \text{HClO}_4, \text{ or "HN(NO}_2)_2"$

$\text{X}^- = \text{NO}_3^-, \text{ClO}_4^-, \text{ or N(NO}_2)_2^-$

For the dinitramide salts, ammonium dinitramide was passed down a strong acid cation exchange resin producing the acid form of dinitramide " $\text{HN(NO}_2)_2$ " which was eluted into a dilute methanolic solution of ethylene bis(oxyamine). In all cases but one, crystalline materials were recovered in high yields and purities. The double dinitramide was recovered as a viscous ionic liquid that we were unable to recrystallize even upon long periods of standing or through repeated thermal cycling.

Several forms of spectroscopy were used to characterize the new family of salts.  $^1\text{H}$  and  $^{13}\text{C}$  spectra revealed small downfield shifts (protonated amine shifts significantly mitigated by the use of  $\text{CD}_3\text{OD}$ ) for the oxyamine proton environment. The starting material had a broad singlet at +4.94 ppm for the  $-\text{O-NH}_2$  environment. A broad singlet for the  $-\text{O-NH}_2$  and  $-\text{O-NH}_3^+$  proton was observed between 5.01 to 5.09 ppm downfield (tms = 0 ppm) for both the monoprotated and diprotated ethylene bis(oxyamine) species. The corresponding proton environments for both the  $\text{CH}_2$  groups of the ethane background appeared as a sharp singlet observed between 4.08 to 4.33 ppm downfield in both the mono as well as diprotated species. In the  $^{13}\text{C}$  spectra the lone carbon signal was in essentially the same region as that of the starting material, an average of 75.0 ppm

downfield while for the monoprotonated species, and an average of 73.5 ppm for the doubly protonated species, which is slightly upfield from the both the monoprotonated as well as the neutral. These peak shifts have been noted before in many other amine systems<sup>11, 12</sup>, and can be mainly attributed to the loss of electron density in the oxyamine group by protonation.

Vibrational spectroscopy strongly supported the expected structures of both the monoprotonated and the double protonated oxyamine salts. Most of the anion bands found in the new salts matched well with the known frequency values for the anions in other well-studied cation-anion systems. The nitrate anion,  $\text{NO}_3^-$ , usually has a strong stretch at  $1345\text{ cm}^{-1}$  in the infrared and a strong band around  $1043\text{--}1050\text{ cm}^{-1}$  in the Raman spectrum.<sup>13, 14</sup> The perchlorate anion,  $\text{ClO}_4^-$ , has a strong broad stretch centered around  $1119\text{ cm}^{-1}$  in the infrared spectra, and strong bands at  $958\text{ cm}^{-1}$  and  $459\text{ cm}^{-1}$  in the Raman spectrum.<sup>15, 16</sup> The dinitramide anion,  $\text{N}(\text{NO}_2)_2^-$ , has strong stretches in the infrared spectrum at around  $1530\text{ cm}^{-1}$ ,  $1445\text{ cm}^{-1}$ ,  $1345\text{ cm}^{-1}$ ,  $1183\text{ cm}^{-1}$ , and  $1025\text{ cm}^{-1}$ , and strong bands in the Raman at  $1335\text{ cm}^{-1}$  and  $830\text{ cm}^{-1}$ .<sup>17-20</sup>

It has been noted that in many amine and hydrazine systems, that upon protonation of a terminal amine functional group,  $-\text{NH}_2$  to  $-\text{NH}_3^+$ , there is drop in the protonated amine N-H stretching frequencies, with a corresponding increase in adjacent C-H stretching frequencies.<sup>21-23</sup> There is also the appearance of a large broad band ranging from  $2400\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$  due to  $\text{R}_3\text{N}^+-\text{H}\cdots\text{X}^-$  hydrogen bonding interactions, which has been observed in other protonated nitrogen systems.<sup>24-26</sup> In the monoprotonated systems there are blue shifts in the unprotonated oxyamine  $-\text{O}-\text{NH}_2$  asymmetric and symmetric N-H stretch frequencies. On average an  $40\text{--}100\text{ cm}^{-1}$  increase for the unprotonated oxyamine N-H asymmetric and symmetric stretch frequencies was observed from those in the starting material and is typical of shifts observed for unprotonated amine groups in other monoprotonated diamine systems.<sup>27</sup> In both singly or doubly protonated species the effect of amine protonation is noted by the appearance of a large, broad diffuse band from  $2400\text{--}2800\text{ cm}^{-1}$  (as noted above for  $-\text{NH}_3^+$  inter and intra molecular hydrogen bonding). In the doubly protonated species, both in the ir and Raman spectra, the complete disappearance of  $-\text{NH}_2$  stretches in the  $3200\text{--}3350\text{ cm}^{-1}$  region was noted along with the appearance of the large diffuse band noted above from  $2400\text{--}2800$

$\text{cm}^{-1}$ . In other alkyl amine systems it has been noted that there is a shift in adjacent  $-\text{CH}_2$  stretching frequencies upon protonation of the amine group.<sup>24-26</sup> In this family of materials, despite that there is an intervening oxygen atom between the amine and the ethylene group, the effect is still apparent in the Raman spectra with the  $-\text{CH}_2$  stretching frequencies shifting an average of  $10\text{--}20\text{ cm}^{-1}$  higher for both the asymmetric as well as symmetric C-H stretches. This observed trend agrees well with observations in prior amine systems<sup>24-26</sup>.

### Crystal Structure Details

Suitable single crystals of ethylene bis(oxyamine) monoperchlorate were grown from methanol solutions carefully layered with diethyl ether and chilled for several days. The structure reveals the expected molecules, however significant hydrogen bonding plays a significant role in the overall geometry of the cation (Figure 1)<sup>28</sup>.

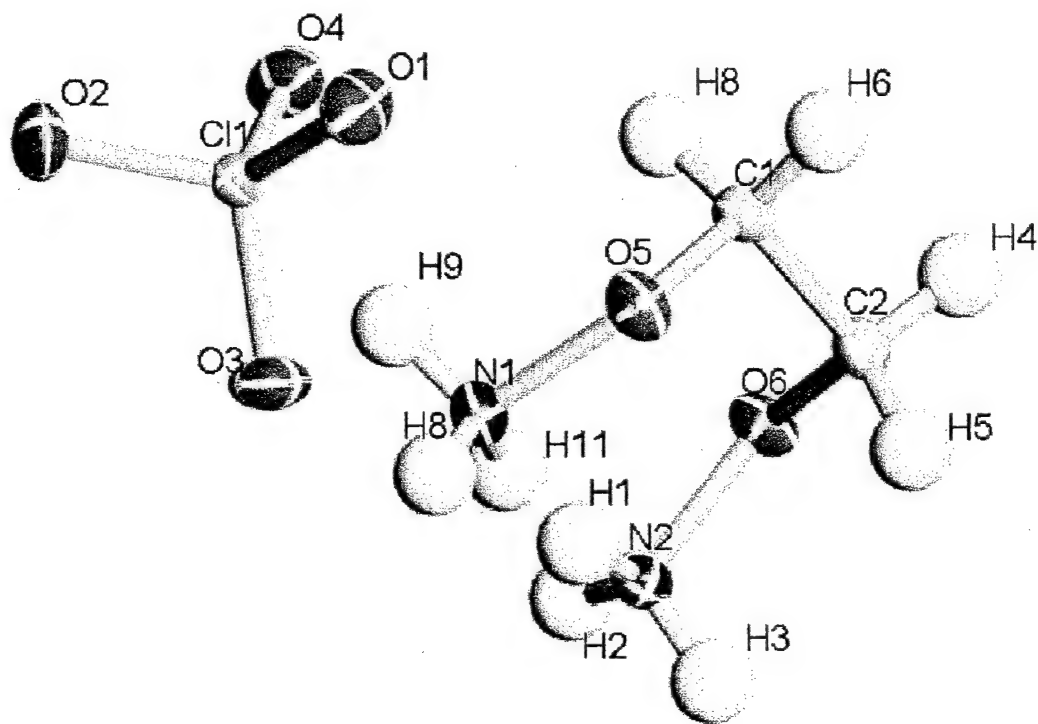


Figure 1. Single crystal x-ray diffraction study revealing the ethylene bis(oxyamine) monocation "horseshoe" structure along with one perchlorate counterion. Atoms H1 and H8 are 30% and 70% occupancy respectively.

The bond distances in both the cation and anion are typical for single bonds and are listed in Table 1. The proton is shared between the terminal amine sites, N(1)-H(11) and N(2)-H(1) (30/70 % partial occupancy) which explains the ring like structure.

<b>Ethylene Bis(oxyamine) mono-perchlorate bond distances in angstroms (Å)</b>		
Cl(1)-O(1) 1.4363(11)	Cl(1)-O(2) 1.4398(11)	Cl(1)-O(3) 1.4368(11)
Cl(1)-O(4) 1.4432(11)	O(5)-N(1) 1.4496(15)	O(5)-C(1) 1.4308(16)
O(6)-C(2) 1.4490(16)	O(6)-N(2) 1.4199(15)	C(1)-C(2) 1.5111(19)
C(1)-H(6) 0.946(16)	C(1)-H(7) 0.974(15)	C(2)-H(4) 0.944(18)
C(2)-H(5) 0.934(16)	N(1)-H(8) 0.89(2)	N(1)-H(9) 0.88(2)
N(1)-H(11) 0.78(9)	N(2)-H(2) 0.87(2)	N(2)-H(3) 0.871(17)
N(2)-H(1) 0.88(2)		

Table 1. Bond distances in ethylene bis(oxyamine) monoperchlorate.

There is a large amount of both inter and intramolecular hydrogen bonding in the cation and anion. The overall shape of the cation is obviously strongly influenced by the intramolecular hydrogen bonding with the overall shape of the cation being one of horseshoe shaped six membered ring structure. (Figure 2) Several of the  $\text{-NH}_3^+ \cdots \text{H}_2\text{N-}$  intramolecular contact are well within the Van der Waal radii sum<sup>29</sup> and are summarized in Table 2. There is also significant interactions between the lone pairs on the linking oxygen atoms and the amine hydrogen atoms. In addition, there are several significant cation anion interactions ( $\text{-NH}_3^+ \cdots \text{O-ClO}_3^-$ ) contacts that are less than the sum of the Van der Waal radii distances which are listed as well.

Overall, hydrogen bonding significantly affects the observed structure and is somewhat unexpected. This would also account for the unusually high density observed in the x-ray structure of  $1.83 \text{ g/cm}^3$  despite the large mole percentage of hydrogen present. Comparisons of observed bond distances with those theoretically predicted reveal the accuracy of the predicted results.

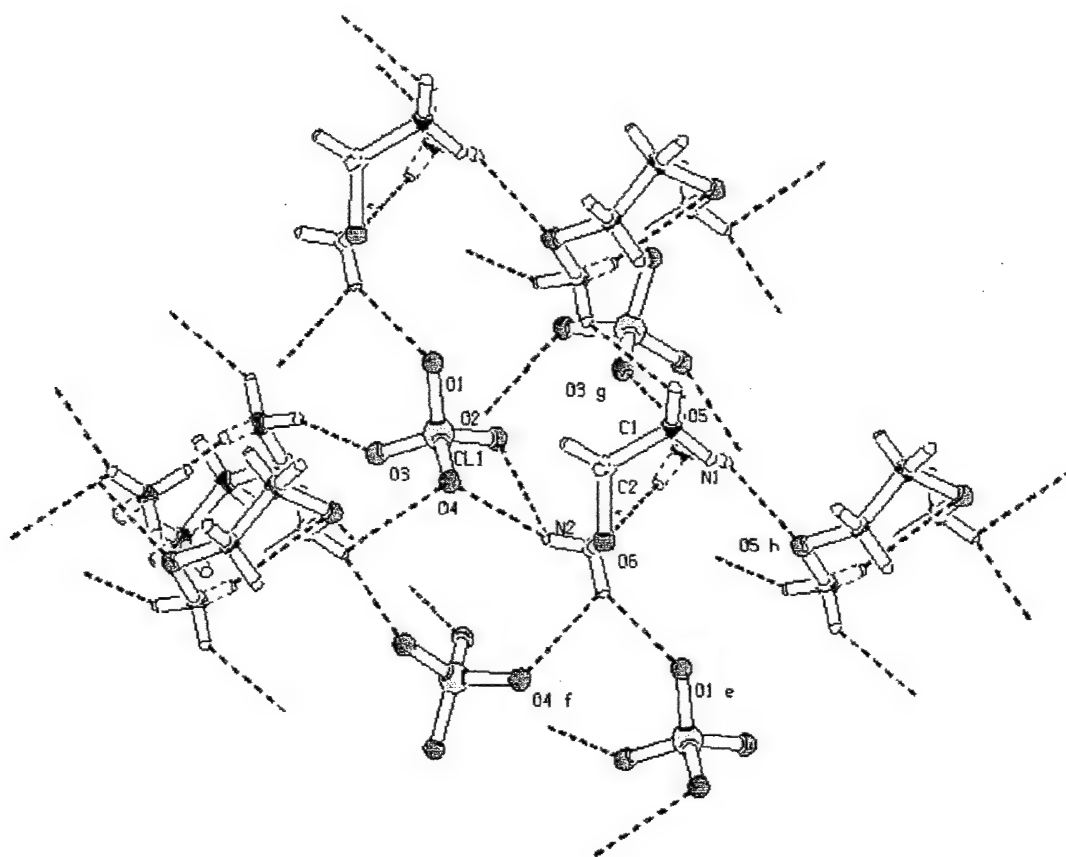


Figure 2. View of the complex inter- and intramolecular hydrogen bonding present in the crystal structure of ethylene bisoxamine monoperchlorate.

Strong H-X interaction	Corresponding H-X bond length (Å)	Interatomic Distance (Å)	Interatomic Distance Between (X-X)	Interatomic Angle (X-H-X)	Symmetry Code
N2 -- H1 .. O5	0.88(2)	2.62(2)	3.310(2)	136(2)	x, y, z
N2 -- H1 .. N1	0.88(2)	1.81(2)	2.674(2)	166(2)	x, y, z
N2 -- H2 .. O1	0.87(2)	2.11(2)	2.874(2)	146(2)	x, 1+y, z
N2 -- H2 .. O4	0.87(2)	2.53(2)	3.006(2)	115(2)	3/2-x, 1/2+y, z
N2 -- H3 .. O2	0.87(2)	2.54(2)	3.155(2)	128(1)	x, y, z
N2 -- H3 .. O4	0.87(2)	2.30(2)	3.063(2)	146(2)	x, y, z
N2 -- H3 .. O3	0.87(2)	2.67(2)	3.231(2)	123(1)	3/2-x, 1/2+y, z
N1 -- H8 .. O3	0.89(2)	2.20(2)	3.028(2)	155(2)	1/2+x, 1/2-y, 1-z
N1 -- H9 .. O5	0.88(2)	2.35(2)	3.100(2)	143(2)	5/2-x, 1/2+y, z
C2 -- H4 .. O1	0.94(2)	2.56(2)	3.335(2)	139(1)	2-x, 1/2+y, 1/2-z
C2 -- H4 .. O5	0.94(2)	2.64(2)	3.428(2)	141(1)	-1/2+x, y 1/2-z
C2 -- H5 .. O4	0.93(2)	2.54(2)	3.270(2)	135(1)	x, y, z

Table 1. Significant intermolecular contacts in the extended structure of ethylene bis(oxyamine) monopерchlorate.

### Differential Scanning Calorimetry (DSC) and Initial Safety Studies

The new materials were evaluated by DSC, which found both the melting point as well as decomposition onset. These studies give the chemist a good idea of general material stability. From Table 3 it can be seen that all of the materials had well-defined melts followed by a short liquidous range whereupon decomposition occurs rapidly and in a highly exothermic manner. This behavior of the ethylene bisoxyamine salts mimicked that observed earlier in the methylene bisoxyamine series<sup>5</sup> and was a disappointment for finding stable materials.



New Salt	Melting point (°C)	Decomposition onset (°C)
$\text{H}_2\text{N-O-CH}_2\text{-CH}_2\text{-O-NH}_2$	125-134	134
$[\text{H}_2\text{N-O-CH}_2\text{-CH}_2\text{-O-NH}_3^+][\text{NO}_3^-]$	73-76	80
$[\text{H}_2\text{N-O-CH}_2\text{-CH}_2\text{-O-NH}_3^+][\text{ClO}_4^-]$	134-137	137
$[\text{H}_2\text{N-O-CH}_2\text{-CH}_2\text{-O-NH}_3^+][\text{N}(\text{NO}_2)_2]$	57-59	75-80
$[\text{H}_3\text{N-O-CH}_2\text{-CH}_2\text{-O-NH}_3^{2+}][\text{NO}_3^-]_2$	130-135	150
$[\text{H}_3\text{N-O-CH}_2\text{-CH}_2\text{-O-NH}_3^{2+}][\text{ClO}_4^-]_2$	122-127	190
$[\text{H}_3\text{N-O-CH}_2\text{-CH}_2\text{-O-NH}_3^{2+}][\text{N}(\text{NO}_2)_2]_2$	< 0	115-120

Table 3. Melting and decomposition onsets for all ethylene bisoxyamine salts.

A point of interest which appears to hold not only for bis(oxyamine) structures discussed here but also the previously described methylene bis(oxyamine) family of materials<sup>x</sup>, is that the neutral (unprotonated) forms of the bis(oxyamines) are extremely stable at ambient temperatures, with storage time of several years with no observable decomposition. However, protonated versions of bisoxyamines whether mono- or di-, have resulted in significant instabilities of the resultant salts. Several of the ethylene bisoxyamine salts began to discolor upon standing even under drybox conditions following the behaviour of methylene bisoxyamine salts<sup>5</sup>. This contrasts significantly to mono- oxyamines such as hydroxyl-amine or methoxyamine which are quite unstable in their anhydrous neat state at ambient conditions<sup>30</sup>, but their corresponding protonated salts can be purchased and stored indefinitely at ambient conditions.

Initial safety studies were carried out with the ethylene bisoxyamine salts. Impact testing was carried out on an Olin Mathieson style drop weight tester where a small sample (20 mg) was placed in a steel cup and a two kilogram mass was dropped vertically upon a closed sample. The minimum drop height in centimeters was recorded for five consecutive negative tests. A sample of five micron 1,3,5,7-tetranitrazacyclooctane (HMX) was used as a standard giving a value of 34 kilogram centimeters. For friction testing, a Julius Peters style friction tester was employed whereby a small amount of sample (20 mg) was placed on a small ceramic square plate,

and steel pin was pushed across the sample under a known load. Any evidence for discoloration, odor, smoke, or spark was considered a positive test. The results are shown in Table 4. In almost all cases, ethylene bis(oxyamine) salts are extremely sensitive to impact and friction, often with quite spectacular results being observed, including loud responses, the shearing of the entire steel pin apparatus on both the drop weight tester and friction tester. This warrants that any handling or manipulations should be carried out in a safe manner as all of the materials are quite hazardous.

New Salt	Drop height (kgcentimeters)	Friction force (kilograms)
$[\text{H}_2\text{N-O-CH}_2\text{-CH}_2\text{-O-NH}_3^+][\text{NO}_3^-]$	94	22.8
$[\text{H}_2\text{N-O-CH}_2\text{-CH}_2\text{-O-NH}_3^+][\text{ClO}_4^-]$	<<20*	<0.45*
$[\text{H}_2\text{N-O-CH}_2\text{-CH}_2\text{-O-NH}_3^+][\text{N}(\text{NO}_2)_2^-]$	28	1.5
$[\text{H}_3\text{N-O-CH}_2\text{-CH}_2\text{-O-NH}_3^{2+}][\text{NO}_3^-]_2$	<<20	Not tested
$[\text{H}_3\text{N-O-CH}_2\text{-CH}_2\text{-O-NH}_3^{2+}][\text{ClO}_4^-]_2$	<<10*	<0.45*
$[\text{H}_3\text{N-O-CH}_2\text{-CH}_2\text{-O-NH}_3^{2+}][\text{N}(\text{NO}_2)_2^-]_2$	<<20	<0.45*

Table 4. Safety test results for ethylene bis(oxyamine) salts. Values with an “\*” had a highly explosive response destroying the striker or scratcher completely.

## Conclusions

A large new family of highly oxygenated salts using ethylene bis(oxyamine) as a starting material were synthesized and fully characterized using mass balance, multinuclear nmr and vibrational spectroscopy, DSC and initial safety testing. Computational results using xxx level of theory revealed structures and spectra that agreed fairly well with those experimentally observed. Initial safety testing revealed an extremely sensitive set of materials regardless of the oxyanion or the degree of protonation.

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### References Cited.

1. Tamura, Y. ; Minamikawa, J. ; Ikeda, M. Synthesis **1977**, 1, 1.
2. Carpino, L. J. Amer. Chem. Soc. **1960**, 82, 3133.
3. Sheradsky, T. Tett. Lett. **1968**, 1909.
4. Marmer, W. ; Maerker, G. J. Org. Chem. **1972**, 37, 3520.
5. Tollison, K. ; Drake, G. ; Hawkins, T. ; Brand, A. ; McKay, M. ; Ismail, I. ; Merrill, C. ; Petrie, M. ; Bottaro, J. ; Highsmith, T. ; Gilardi, R. J. Energetic Mater. **2001**, 29, 277.
6. P. Wasserscheid; T. Welton Ionic Liquids in Synthesis Wiley-VCH Verlag, GmbH & Co. Weinheim, Federal Republic of Germany, **2003**, pg 1.
7. Zhao, H. ; S.V. Malhotra Aldrichimica Acta **2002**, 35, 3, 75.
8. W. Keim ; P. Wasserscheid Angew. Chem. Int. Ed. Engl. **2000**, 39, 3772
9. Wilkes, J. Green Chemistry **2002**, 4, 3.
10. Dixon, D ; Weiss, R. J. Organ. Chem. **1984**, 49, 4487.
11. Pouchert, C. J. The Aldrich Library of NMR Spectra Edition II, Volume 1. **1983**, Aldrich Chemical Company, Inc., Milwaukee, Wisconsin.
12. Simmons, W. W. (Ed.) The Sadtler Guide to Carbon-13 NMR Spectra. **1983**, Sadtler Research Laboratories, Philadelphia, PA.
13. Williamson, K. ; Li, P. ; Devlin, J. P. J. Chem. Phys. **1968**, 48, 3891.
14. Nakagawa, I. ; Walter, J. L. J. Chem. Phys. **1969**, 51, 1389.
15. Cohn, H. J. Chem. Soc. **1952**, 4282.
16. Redlich; Holt; Biegeleisen J. Amer. Chem. Soc. **1944**, 66, 13.
17. Bottaro, J. L. ; Penwell, P. E. ; Schmitt, R. J. Synth. Commun. **1991**, 21, 945.

18. Bottaro, J. L. ; Schmitt, R. J. ; Penwell, P. A. ; Ross, D. S. U. S. Patent 5198204, 1993.
19. Shylapochmikov, V. A. ; Oleneva, G. I. ; Cherskayas, N. O. ; Luk'yanov, O. A. ; Gorelik, V. P. ; Anikin, O. V. ; Tartakovsky, V. A. Izv. Akad. Nauk. Ser. Khim. 1995, 1508.
20. Christe, K. O. ; Wilson, W. W. ; Petrie, M. A. ; Michels, H. H. ; Bottaro, J. C. ; Gilardi, R. Inorg. Chem. 1996, 35, 5068.
21. Garfinkel, D. ; Edsall, J. T. J. Amer. Chem. Soc. 1958, 80, 3823.
22. Ghazanfar, S. A. S. ; Edsall, J. T. J. Amer. Chem. Soc. 1964, 86, 559.
23. Garfinkel, D. ; Edsall, J. T. J. Amer. Chem. Soc. , 1958, 80, 3807.
24. Bellanato, J. Spectrochim. Acta 1960, 16, 1344.
25. Edsall, J. T. ; Scheinberg, H. J. Chem. Phys 1940, 8, 520.
26. Chenon, B. ; Sandorfy, C. Can. J. Chem. 1958, 36, 1181.
27. Ghazanfar, S. A. S. ; Edsall, J. T. ; Myers, D. V. J. Amer. Chem. Soc. 1964, 86, 559.
28. Crystal structure details for ethylene bis(oxyamine) monoperchlorate: Empirical Formula  $C_2H_9N_2O_6Cl$ ; Formula weight: 192.56; Crystal system: orthorhombic; space group: Pbca (No. 61); Unit cell dimensions (angstroms):  $a = 10.0689(18)$ ,  $b = 7.5231(14)$ ,  $c = 18.679(3)$ ; Volume =  $1414.9(4) \text{ \AA}^3$ ;  $Z = 8$ ;  $D(\text{calculated, g/cm}^3) = 1.808$ ;  $\mu = 0.532 \text{ mm}^{-1}$ ;  $F(000) = 800$ . Data collection: Temperature = 173K; Mo  $K\alpha$  radiation  $0.71073 \text{ \AA}$ ; Theta (min – max; degrees) =  $2.2 \leq \Theta \leq 28.3$  ; hkl – 10:12; -9:8; -19:24 ; Total reflections = 8120; Unique reflections = 1671;  $R(\text{int.})0.034$ ; Observed data [ $I > 2\sigma(I)$ ] = 1560; Refinement Number of reflections = 1671, number of parameters = 142;  $R = 0.284$ ,  $wR2 = 0.752$ ,  $s = 1.05$ ; Minimum and maximum residual electron density ( $e/ \text{\AA}^3$ ) = -0.43 to 0.35.
29. Van der Waal radii paper.
30. Organic Synthesis volume.